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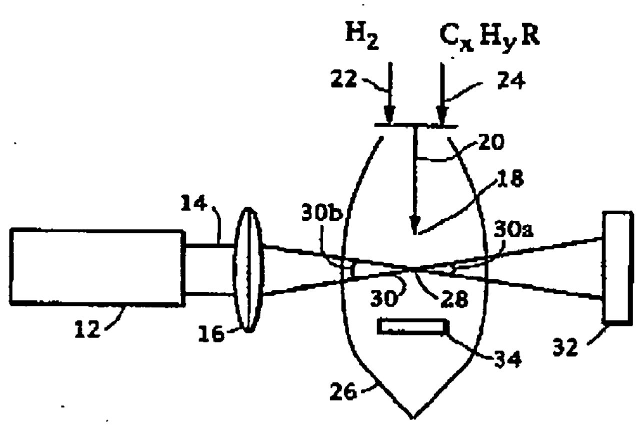
(54) Title: LASER ABSORPTION WAVE DEPOSITION PROCESS



(57) Abstract

There is disclosed herein a pulsed laser method for forming film coatings from a gas, such as H_2 (22) and a hydrocarbon (24). The gas mixture input by line (20) and nozzle (18) is ignited by laser (12) to form flame (26) and then irradiated by a laser pulse (14) at an energy level above the threshold breakdown level of the gas to create a seed plasma in the gas at (28). Subsequent energy from the laser pulse is absorbed to form a plasma excitation called a laser absorption wave (30). The laser absorption wave is a wall of energy which detaches from the seed plasma and propagates through the gas (30a, b). The film growth precursor fragments of the gas are generated by the laser absorption wave and deposited onto a substrate (32 or 34) welding to its surface to form a coating. The substrate surface may be partially liquefield or evaporated forming precursor fragments of the substrate that mix with the precursor fragments of the gas that weld to the substrate forming a coating.

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LASER ABSORPTION WAVE DEPOSITION PROCESS

BACKGROUND OF THE INVENTION

FIELD OF THE INVENTION

Diamond coatings are in great demand as protective coatings for number of materials, as hardness coatings on various machine tools, and as electronic materials, owing largely to the qualities of high thermal conductivity, electron mobility, and radiance resistance. Furthermore, diamond also finds application as a cold cathode material due to its high, negative electron affinity. Such cold cathode applications will make possible flat panel displays and is identified as an excellent drug delivery system due to its chemical inertness, lack of biodegradation, and the ability of various organic molecules to reversibly bind to its surface.

Because of the great demand, techniques have been developed to apply diamond coatings to a wide variety of materials. Common to all the production techniques is the formation of a plasma as a source of atomic hydrogen and diamond precursors. Conventional chemical vapor deposition methods require substrate heating to temperatures between 800 to 1000° C. as well as low gas pressures to tens of torr to ensure the diffusion of material from the plasma to a solid state target substrate. In the case where diamond growth takes place at atmospheric pressure, using the flame techniques pioneered by Hirose, substrates tend to over heat beyond the desirable substrate temperatures, thus requiring the active cooling of the target substrate, Alternately, pressures of tens of thousands of atmospheres and thousands of degrees are used to create high pressure, high temperature diamond within molten acetylide salts.

In U. S. Patent 4,981,717 assigned to the assignee of the instant application, there was disclosed a method of depositing diamond coatings wherein the method generated a plasma by absorption of the laser radiation into a precursor gas or a gas mixture at atmospheric pressure. The laser pulse is absorbed by the initiator gas which is mixed in with precursor gases such as hydrocarbon, for example, methane, ethane propane, ethylene, acetylene. The initiator is preferably a compound which is strongly absorbing at the output wavelength of the laser pulse

which is strongly absorbing at the output wavelength of the laser pulse used. The shock wave associated with the sudden absorption of laser radiation was utilized in transporting ions radicals, and molecular fragments onto a suitably positioned substrate The diamond like coatings formed were of a carbonaceous species having characteristics of hardness and chemical structure similar to diamond.

SUMMARY OF THE INVENTION

There is provided by this invention a general pulsed laser method for forming film coatings from a gas phase. A seed plasma is created in the gas via an intense, focused laser pulse forming an initiating material. Subsequent energy from the laser pulse is absorbed to form a plasma excitation called a laser absorption wave. The laser absorption wave is a wall of energy which detaches from the seed plasma and propagates through the gas. The film growth precursors are generated by the laser absorption wave onto a substrate welding to its surface to form a coating. The substrate surface is partially liquefied or evaporated allowing the coating materials to weld to the substrate.

BRIEF DESCRIPTION OF THE DRAWINGS

FIGURE 1 is a schematical diagram of apparatus for performing the laser deposition process incorporating the principles of the inventions herein;

FIGURE 1A is alternate embodiment of the schematical diagram shown in FIGURE 1 having a substrate reflective of the laser beam;

FIGURE 2 is a schematical diagram of apparatus for the laser deposition process having a substrate transmissive to the laser beam;

FIGURE 3 is a schematical embodiment of the laser deposition process illustrating ablation of the substrate;

FIGURE 3A is an alternate embodiment of the ablation process shown in FIGURE 3; and

FIGURE 4 is a schematical embodiment of the laser deposition process illustrating laser heating of the substrate.

BRIEF DESCRIPTION OF THE PREFERRED EMBODIMENT

There is shown in FIGURE 1 the laser absorption wave apparatus 10 that is generally comprised of a laser 12 that emits a laser pulse 14 that is focused by a lens 16 into a gas stream emitting from the nozzle 18. The gases emitted from the nozzle 18 are combined in the gas line 20 that is supplied by gases from a hydrogen input 22 and a hydrocarbon gas input 24. The hydrocarbon gas maybe any gas containing the fragment having the chemical formula C_xH_y. The irradiation of the gas by the laser ignites a flame 26 and above threshold levels for avalanche breakdown creates an electron seed plasma at 28. The flame 26 also serves to heat the substrate. It should be noted here that in some applications the process herein described is performed in a closed chamber filled with an inert gas to eliminate the flame 26. Further excitation by the laser creates a laser absorption wave generally shown at 30. The pulse width of the laser is adjusted to deliver additional energy to the seed plasma beyond the threshold level for avalanche breakdown. Gas behind the plasma at 30a is cut off from the laser source, while the newly formed plasma layer at 30b can absorb most of the incident laser energy. This absorbed energy is converted to an ionization shock wave, ionizing successive layers of gas, which in turn optically absorb. The process cascades and the ionization shock wave builds, propagating back toward the laser source. The minor laser absorption wave shown at 30a propagates away from the laser 12 and produces diamond particles on the substrate 32. It can be seen in Figure 1 that the substrate 32 is in the optical path of the laser pulse 14. Depending on the energy level of the laser the surface of the substrate 32 will be evaporated forming a gas supplementing the absorption wave. The evaporated material from the substrate 32 recondenses and is coated by the material generated by the laser absorption wave 30a forming a diamond film on the substrate 32 or substrates in close proximity such as 34. At mid levels of laser energy the substrate of the layer creates a spray of liquid or heated material that act as nucleation centers for accumulating materials generated in the laser absorption wave. At lower energy levels the surface of the substrate 32 is liquefied and the materials created in the absorption wave are welded to the surface of the substrate

32. These particles create a diamond film that resulted from the breakdown of the hydrocarbon gas and hydrogen mixture.

There is shown in FIGURE 1a an alternate method of coating a substrate with a diamond film using the laser absorption wave technique. In this embodiment the substrate 32 is reflective. The laser pulses 14 from the laser are focused on the substrate such that reflective pulses 36 initiate the laser absorption wave 30. In this configuration, energy from the laser pulses 14 are used partially to preheat the substrate 32 and the laser absorption wave is created with the balance of the energy such that the major portion of the wave 30b is now propagating toward the substrate 32. This enhances the diamond deposition rate on the substrate.

Referring to FIGURE 2 there is shown a further embodiment incorporating the principles of using a laser absorption wave to deposit diamond on substrates. In this configuration, a substrate 38 is inserted between the laser and the laser absorption wave 30. The substrate 38 is transmissive such that once the laser absorption wave is initiated the major portion of the laser absorption wave 30b travels in the direction of the substrate 38 and coats the substrate 38. It should be appreciated in all of the embodiments shown that both composition and phase of the deposit on the substrate may be changed by variation of the process parameters such as the focal standoff, the distance between the focal point of the laser and the substrate; the laser pulse energy; the laser pulse repetition rate; and the flow rates of the gases. The following table lists examples of process parameters for various substrates:

Substrate	z (mm)	E_L(mJ)	f_{H2}	f_{CH4}	T_s	cell
tungsten carbide	-12	100	15	0.04	800°	Open
440C steel	0	300	15	0.04	800°	Open
440C steel	+22	75	30	0.04	30°	Closed
graphite (POCO)	0	100	27	0.04	30°	Closed
aluminum (2024)	+15	300	17	0.20	30°	Closed
titanium (Ti-6-AR-AV)	+20	75	12	0.04	30°	Closed
silicon	-10	150	12	0.04	30°	Closed

In the table above z = the standoff distance in millimeters where positive standoff is shown in figure 1 and negative standoff is shown in figure 2; E_L = th laser pulse energy in millijoules; f_{H2} = flow rate of hydrogen in liters per minute; f_{CH4} = flow rate of methane in liters per minute; T_s = bulk substrate temperature in degrees centigrade; and cell indicates whether the process was conducted in open air with flame or closed chamber without flame. The proces was performed with a YAG laser, Q-switched at 1.06 µm, 10 nsec spike, with a repetition rate = 20 Hz. The lens was a f4 focusing lens with a 6" focal length.

FIGURE 3 illustrates a further embodiment where the pulses 14 of the laser 12 are focused by the lens 16 onto the target 32 such that the area of substrate liquifies or evaporates to produce an atomized spray or liquid or a solid seed 40. Under conditions where temperature of the individual nuclei is approximately 800-1200°C, the spray 40 is injected into the laser absorption wave which is simultaneously created. When the target 32 is graphite or a high carbon content material, the spray 40 provides carbon seeds which are coated by the laser absorption wave 30 in a homogeneous nucleation scheme to produce diamond. Material consolidation forms a film on the substrate 32. Further, material arriving within the optical path 42 and consolidating on the transmissive substrate 38 may be used to create an optical coating. Spray nuclei with sufficient momentum to traverse the laser absorption wave 30 through the optical path 42 can create separate particles for use as grit or polishing powder which may be collected on substrate 44.

If the substrate material 32 is a metal, the spray 40 then provides solid or liquid metal nuclei that seed the laser absorption wave 30. In this instance the metal condensates are coated with the diamond. The resulting coated particles may then reconsolidate on a substrate such as 32 to produce a metal diamond composite coating. Such a process is facilitated if the metal is still liquid and hence mobile. Metal nuclei escaping through the laser absorption wave 30 may be coated with diamond to create distinct particles of diamond coated metal. Should such conglomerate particles cool before capture on a substrate 44, perfectly spherical abrasive or bearing particles may be formed. If arriving particles still possess liquid cores, the molten metal serves to weld a diamond metal composite to the substrate 44.

FIGURE 3a teaches an alternate embodiment where the laser pulses 14 are focused directly on the substrate 32 creating the spray 40. The precursive gases of hydrogen and hydrocarbon mix are also supplied at this focal point by the nozzle 18 such that the laser absorption wave now is created at the surface of the substrate. This further enhances seeding of the laser absorption wave 30 for developing the diamond like film.

FIGURE 4 illustrates an alternate embodiment wherein the laser absorption wave apparatus 10 is modified to incorporate a pulse splitter 46 that divides the laser wavefront along a separate optical path 48 such that is it focused by lens 50 upon the substrate 32 so as to preheat it. This configuration wherein part of the laser output pulse is split off to preheat the substrate can be utilized in all of the embodiments hereinabove shown and described.

This process can be used to deposit other films such as SiO_2 with O_2 as the gas and Si as the sacrificial substrate; Si_3N_4 with N_2 as the gas and Si as the sacrificial substrate; amorphic carbon with carbon vapor as the gas and graphite as the sacrificial substrate; and cubic boron nitride and hexagonal boron nitride with N_2 as the gas and hexagonal boron nitride as the sacrificial substrate.

Although there has been illustrated and described a specific structure, it is clearly understood that the same were merely for purposes of illustration and that changes and modifications may be readily made therein by those skilled in the art without departing from the spirit and scope of this invention.

I claim:

1. A method of coating materials comprising the steps of:
   a) Providing a source of gas mixture;
   b) igniting the gas mixture into a flame;
   c) irradiating the ignited gas mixture with a laser pulse at the threshold avalanche breakdown level of the mixture creating a seed plasma within the mixture;
   d) adjusting the laser such that the laser has an energy level at a level above the breakdown level creating a laser absorption wave creating precursor fragments of the gas mixture; and
   e) placing a substrate within close proximity of the laser absorption wave such that the laser absorption wave carries precursor fragments to the substrate wherein the substrate develops a coating comprised of the precursor fragments of the gas mixture.

2. A method of coating materials as recited in claim 1 further comprising the step of focusing the laser at a point into the mixture at a standoff distance which is the distance between the focal point and the substrate to create the seed plasma.

3. A method of coating materials comprising the steps of:
   a) providing a source of gas mixture;
   b) igniting the gas mixture into a flame;
   c) irradiating the ignited gas mixture with a laser pulse above the threshold breakdown level of the mixture creating a seed plasma within the mixture that results in a laser absorption wave in the mixture; and
   d) placing a substrate in the optical path of the laser pulses causing a portion of the substrate to liquefy or evaporate producing a spray or seed plasma of precursor fragments from the substrate that mixes with precursor fragments of the gas mixture in the laser absorption wave wherein the substrate develops a coating comprised of the mixed precursor fragments from the gas mixture and the substrate.

4. A method of coating materials as recited in claim 1 comprising the step of providing substrate that is transmissive of the laser pulse and placing the substrate between the laser and the source of gas mixture.

5. A method of coating materials as recited in claim 1 wherein the gas mixture is comprised of hydrogen and hydrocarbon compounds and the coating is comprised of diamond.

6. A method of coating materials as recited in claim 3 wherein the gas mixture is comprised of hydrogen and hydrocarbon compounds and the coating is comprised of diamond.

7 A method of coating materials as recited in claim 3 wherein the substrate is metallic.

8. A method of coating materials as recited in claim 8 wherein the gas mixture is comprised of hydrogen and hydrocarbon compounds.

9. A method of coating materials as recited in claim 9 wherein metallic nuclei from the substrate are coated with diamond forming diamond microspheres.

10. A method of coating materials as recited in claim 1 wherein the gas mixture is comprised of O_2, the substrate is comprised of Si, and the coating is comprised of SiO_2.

11. A method of coating materials as recited in claim 3 wherein the gas mixture is comprised of O_2, the substrate is comprised of Si, and the coating is comprised of SiO_2.

12. A method of coating materials as recited in claim 1 wherein the gas mixture is comprised of N_2, the substrate is comprised of Si, and the coating is comprised of Si_3N_4.

13. A method of coating materials as recited in claim 3 wherein the gas mixture is comprised of N_2, the substrate is comprised of Si, and the coating is comprised of Si_3N_4.

14. A method of coating materials as recited in claim 1 wherein the gas mixture is comprised of carbon vapor, the substrate is comprised of graphite, and the coating is comprised of amorphic carbon.

15. A method of coating materials as recited in claim 3 wherein the gas mixture is comprised of carbon vapor, the substrate is comprised of graphite, and the coating is comprised of amorphic carbon.

16. A method of coating materials as recited in claim 1 wherein the gas mixture is comprised of N_2, the substrate is comprised of hexagonal boron nitride, and the coating is comprised of cubic boron nitride or hexagonal boron nitride.

17. A method of coating materials as recited in claim 3 wherein he gas mixture is comprised of N_2, the substrate is comprised of hexagonal boron nitride, and the coating is comprised of cubic boron nitride or hexagonal boron nitride.

18. A method of coating materials as recited in claim 1 wherein the laser pulse is divided and a portion of the laser pulse is focused on the substrate to preheat the substrate.

19. A method of coating materials as recited in claim 3 wherein the laser pulse is divided and a portion of the laser pulse is focused on the substrate to preheat the substrate.

20. A method of coating materials comprising the steps of:

a) providing a source of gas mixture;

b) igniting the has mixture into a flame;

c) irradiating the ignited gas mixture with laser pulses having an energy level at the threshold breakdown level of the mixture creating a seed plasma within the mixture;

d) adjusting the laser such that the laser has an energy level above the breakdown level creating a laser absorption wave creating precursor fragments of the gas mixture; and

e) placing a first substrate within close proximity of the laser absorption wave and in the path of the laser pulses causing the first substrate to liquefy or evaporate producing a spray or a second seed plasma of precursor fragments from the substrate that mixes with the precursor fragments of the has mixture in the laser absorption wave, and

f) placing a receiving substrate within close proximity of the first substrate wherein the receiving substrate receives a coating comprised of the mixed precursor fragments from the gas mixture and the first substrate.

21. A method of coating materials as recited in claim 25 further comprising the step of focusing the laser at a point into the mixture at a standoff which is the distance between the focal point and the first substrate to create the second see plasma.

22. A method of coating materials as recited in claim 25 wherein the first substrate is metallic.

23. A method of coating materials as recited in claim 25 wherein metallic nuclei from the first substrate are coated with diamond, forming diamond microspheres.

24. A method of coating materials as recited is claim 25 wherein the laser pulse is divided and a portion of the laser pulse is focused on the substrate to preheat the substrate.

25. A method of coating materials comprising the steps of:

a) providing a source of gas mixture;

b) igniting the gas mixture into a flame;

c) irradiating a reflective substrate with laser pulses having an energy level above the threshold breakdown level of the gas mixture creating a laser absorption wave in the gas mixture after reflection from the substrate and further causing a portion of the substrate to liquefy or

evaporate producing a spray or seed plasma of precursor fragments from the substrate that mixes with precursor fragments of the gas mixture in the laser absorption wave wherein the substrate develops a coating comprised of the mixed precursor fragments from the gas mixture and the substrate.

26. A method of coating materials comprising the steps of:

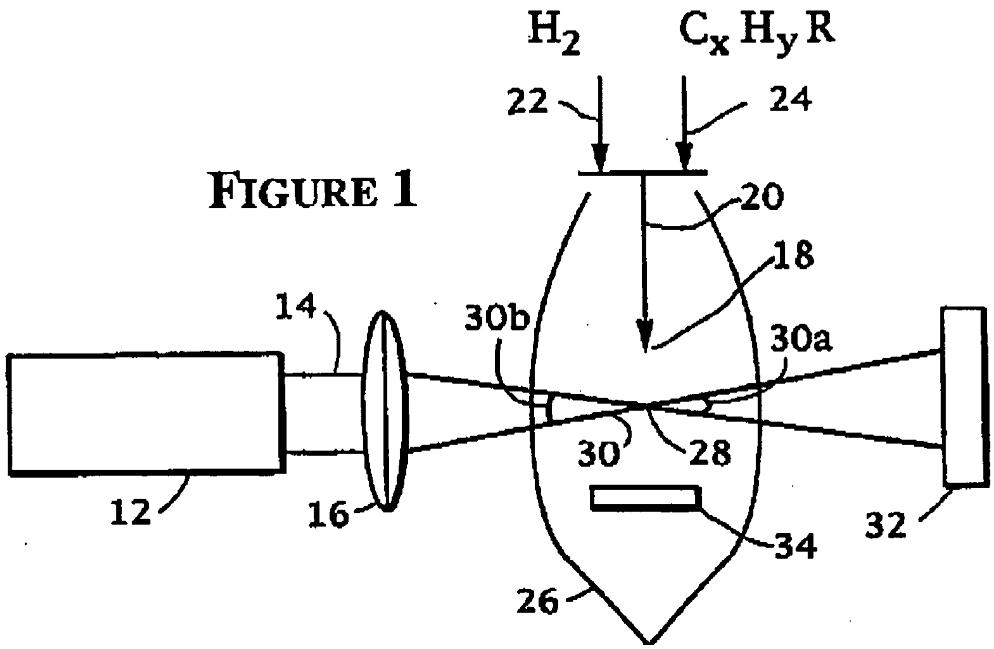
a) providing a source of gas mixture into a closed chamber;

b) irradiating the has mixture with a laser pulse at the threshold breakdown level of the mixture creating a seed plasma within the mixture;

c) adjusting the laser such that the laser has an energy level at a level above the breakdown level creating a laser absorption wave containing precursor fragments of the gas mixture; and

d) placing a substrate within close proximity of the laser absorption wave such that the laser absorption wave carries the precursor fragments to the substrate wherein the substrate develops a coating comprised of the precursor fragments of the gas mixture.

FIGURE 1



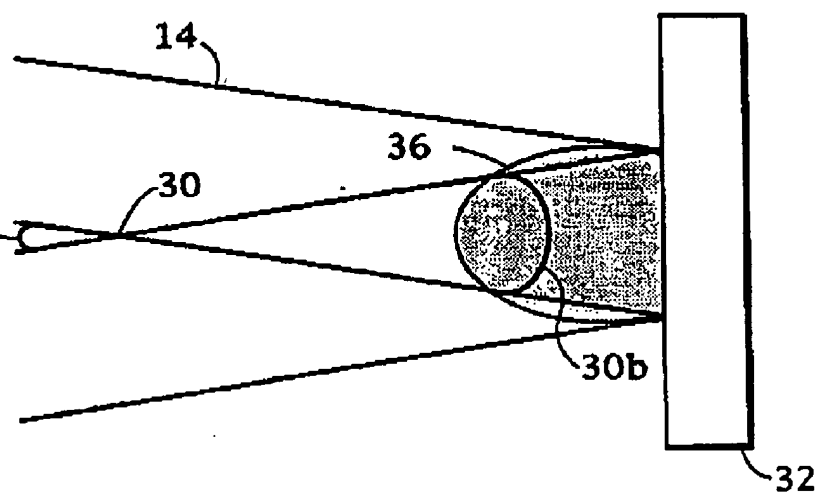


FIGURE 1a

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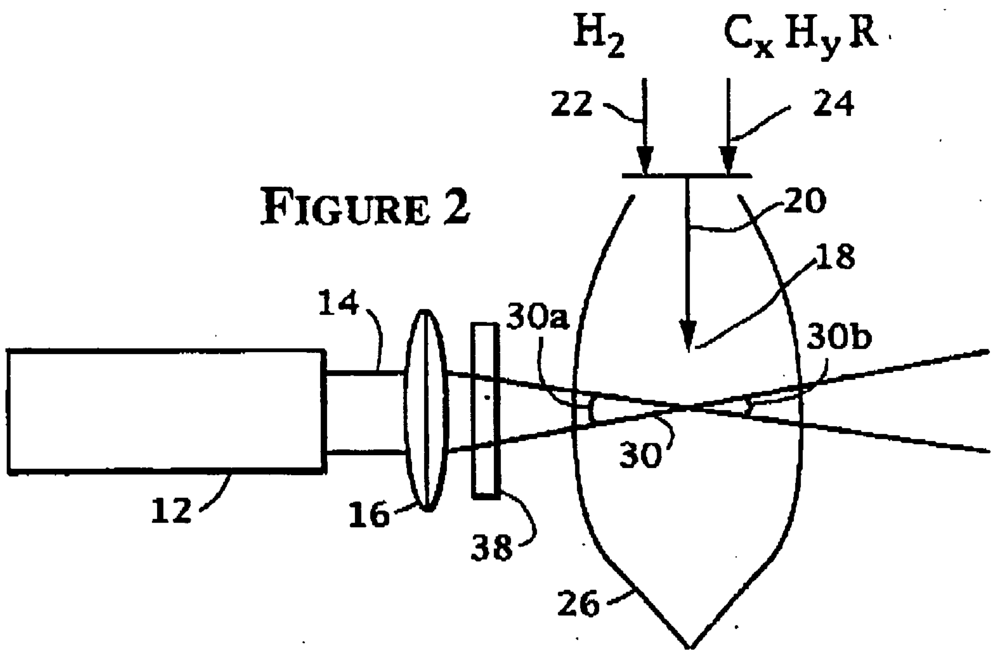

FIGURE 2

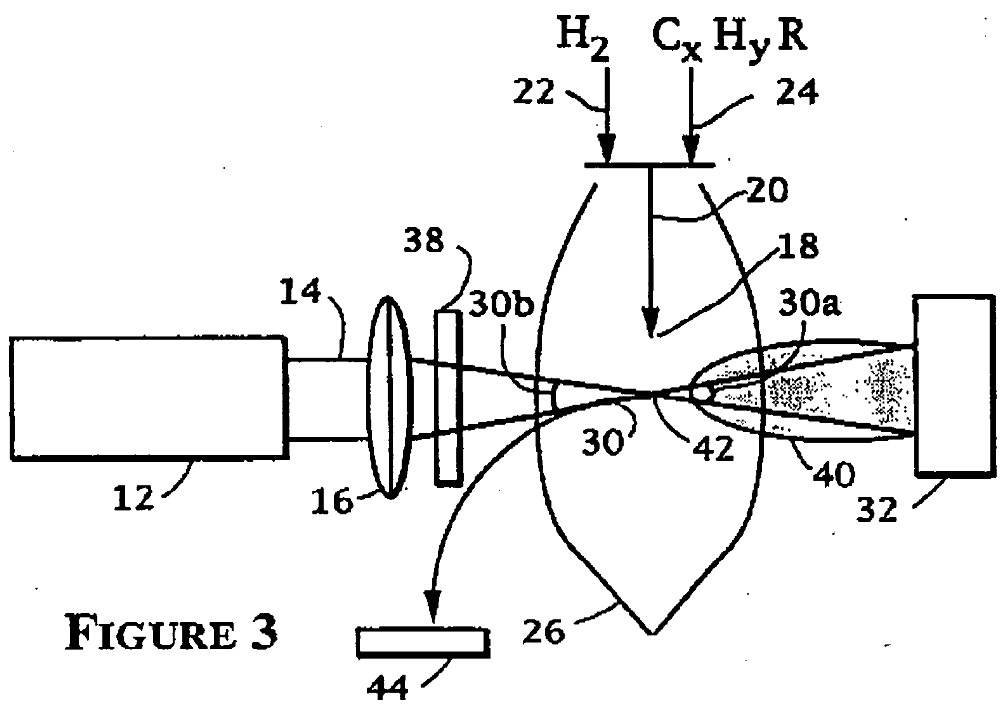

FIGURE 3

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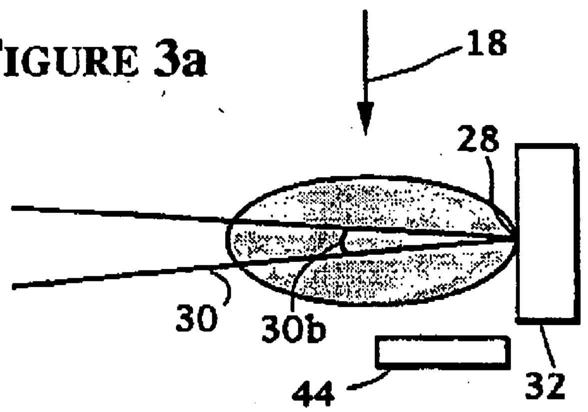
FIGURE 3a



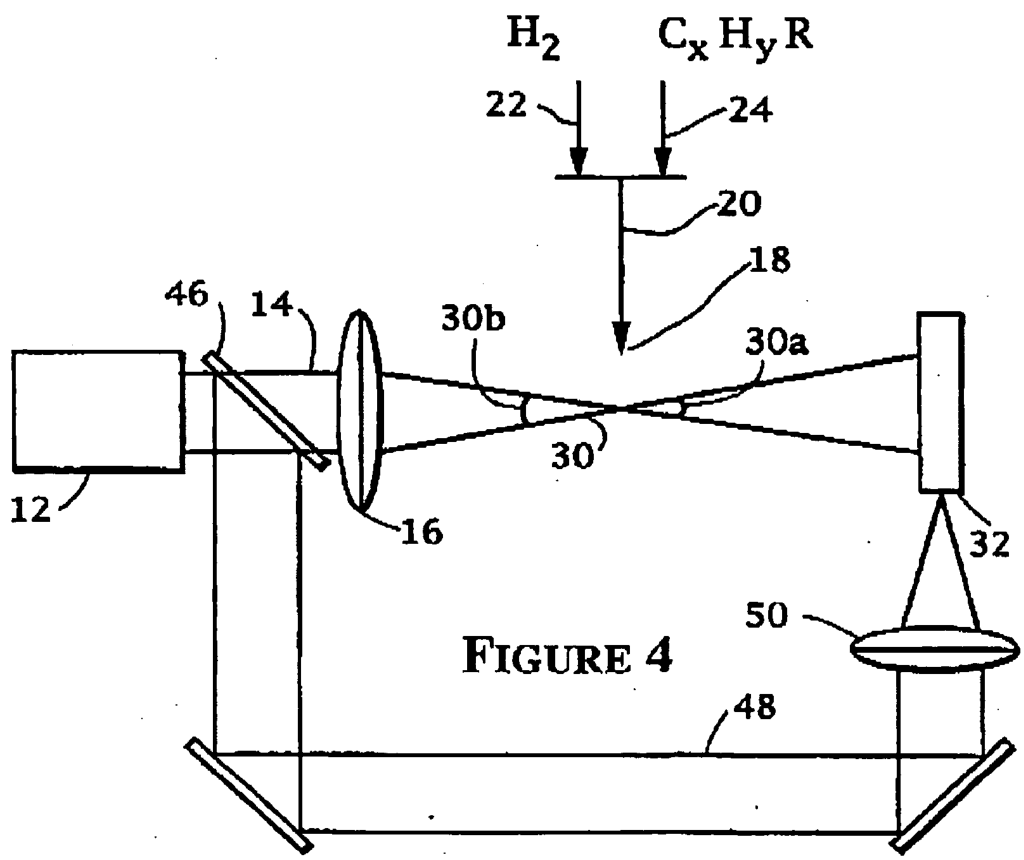


FIGURE 4

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A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) :B05D 3/06, 7/00
US CL :427/561,582,583,584,586,596,597,216
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 427/561,566,582,583,584,586,596,597,554,555,556,216

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	Yu. P. Raizer, Studies in Soviet Science, "Laser-Induced Discharge Phenomena", p.9, 189-192, Consultants Bureau, N.Y. 1977.	1-26
A	John F. Ready, Effects of High-Power Laser Reduction, Academic Press, N.Y. 1971, p. 219-220.	1-26
A	US,A, 4,302,933 (Smith) 01 December 1981.	1-26
A	US,A, 5,149,406 (Mullen et al) 22 September 1992	1-26
Y	US,A, 4,972,061 (Duley et al) 20 November 1990, Abstract; col. 1, lines 45-61; col. 2, lines 46-65; col. 3, lines 49-58 and 63; col. 4, lines 62-63; col. 5, lines 48-64.	1-3,6-9,11-14,19-20,25-27 and 29-31

[X] Further documents are listed in the continuation of Box C. [ ] See patent family annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
12 JULY 1994	01 AUG 1994

Name and mailing address of the ISA/US	Authorized officer
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INTERNATIONAL SEARCH REPORT

Int. :ional application No.
PCT/US94/05319

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Y	US,A, 4,892,751 (Miyake et al) 09 January 1990, abstract; col. 1, lines 34-58; col. 2, lines 12-48 and 35-47, col. 9, lines 42-58; col. 10, lines 8-14; embodiments 2 and 6, Figures.	1-3,6-9,11-14,19-20,25-27 and 29-31
Y,P	US,A, 5,254,832 (Gartner et al) 19 October 1993, col. 4, lines 14-18 and 43-58; Figures.	10,28
Y	US,A, 5,154,945 (Baldwin et al) 13 October 1992, abstract, Figures.	1-3,6-9,14,19-20,25-27 and 29-31
Y	US,A, 5,098,737 (Collins et al) 24 March 1992, claim 1.	15-16
A	US,A, 5,096,739 (Strutt et al) 17 March 1992, abstract, Figures,	1-26
Y	US,A, 5,080,753 (Doll et al) 14 January 1992, col. 3, lines 8-35.	17-18
Y	US,A, 4,537,791 (Tarjan) 27 August 1985, abstract, Figures.	15-16
Y	US,A, 4,248,909 (Whittaker) 03 February 1981, abstract.	15-16
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